MEASUREMENT OF CARBON-CARBON ELECTRICAL CONDUCTIVITY DURING PYROLYSIS

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INTRODUCTION

The eddy current sensor described below is one of several sensors that is currently being used to monitor the pyrolysis of carbon-carbon materials. It is part of a larger system that is being developed for the closed loop control of the carbon-carbon manufacturing process [1]. The eddy current sensor is being used to monitor changes in the electrical conductivity of the specimen.

Carbon-carbon material begins as a composite material that is made from graphite fibers and a phenolic matrix. After the material is laid up, it is cured at 160°C to form a rigid composite that has an external appearance similar to that of a graphite/epoxy composite. This is referred to as the "as cured" state of the carbon-carbon. The part is then pyrolyzed in a retort filled with an inert atmosphere by raising the temperature to 800°C. As the temperature is increased various chemical reactions occur that convert the phenolic to carbon and produce a porous microstructure in the part. After the first pyrolysis cycle, the material is impregnated with phenolic and again pyrolyzed. This procedure is repeated until the material has reached a specified density. We are chiefly concerned with minimizing the time required for a pyrolysis cycle while assuring that the part is not destroyed by a catastrophic failure such as delamination. Since the probability of a delamination occurring is highest during the first pyrolysis cycle, we have been directing our effort towards the monitoring of changes in various material properties during this time.

Prior to the use of eddy currents to make these measurements, two other techniques for measuring electrical conductivity were tried without success. The first was microwave reflectivity measurements. These can be used with the phenolic alone, but are blocked by the high conductivity graphite fibers. The second was a dc measurement technique that required contacts to be attached to the specimen. Although this technique worked well with the phenolic resin, it was not robust in the presence of the graphite fibers because they tended to short out the electrodes.

METHOD FOR MAKING MEASUREMENTS

Figure 1 shows the flat spiral eddy current coil on a carbon-carbon specimen. The fields from the coil will decay with depth into the specimen. The skin depth (or
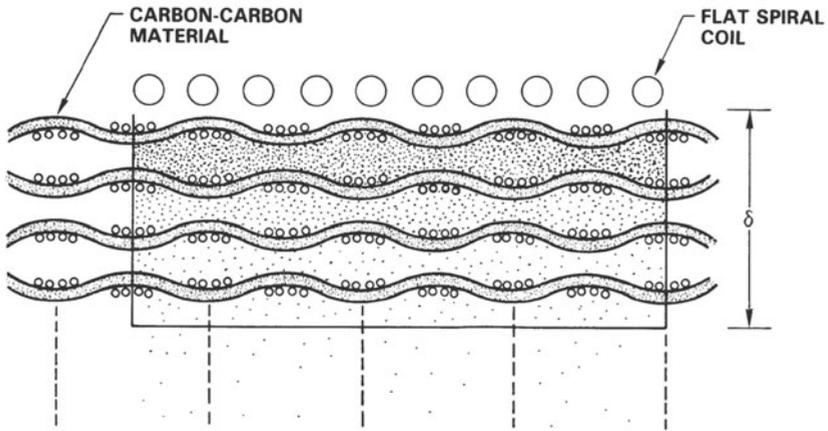
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Fig. 1   Schematic of flat spiral eddy current coil on carbon-carbon specimen with skin depth δ.

1/e distance, designated δ), is adjusted to be approximately equal to the thickness of the specimen by changing the frequency of oscillation of the coil. This frequency was between 4 and 5 MHz for the in situ measurements described here. Since the diameter of the coil is large compared to the weave of the plies, the fields sample a sufficiently large volume that the composition appears to be homogeneous. Thus the precise placement of the coil on the specimen is not critical.

We have chosen to use pulsed excitation of the coil as shown in Fig 2. The coil is simply modeled as an inductor, L_p, and a resistor, R_p. The value of the capacitor that is connected across the coil is adjusted to change the oscillation frequency of the circuit that is excited when it is driven by an impulse. The eddy currents are induced in the specimen and damped by its conductivity. The decaying oscillation is observed on an oscilloscope and digitized for subsequent signal processing.

Figure 3a shows one of the signals produced by the coil. To measure the damping coefficient of the coil plus the eddy currents, this signal is Fourier transformed to produce the spectrum in Fig. 3b. The damping coefficient is obtained from the center frequency of the spectrum and the width of the spectrum at its -6 dB points. The measurement is initially made with the coil suspended in air to obtain the damping coefficient, ζ_0, of the coil alone. The conductivity, G_C, of the carbon-carbon specimen is then obtained from Eq. (1).
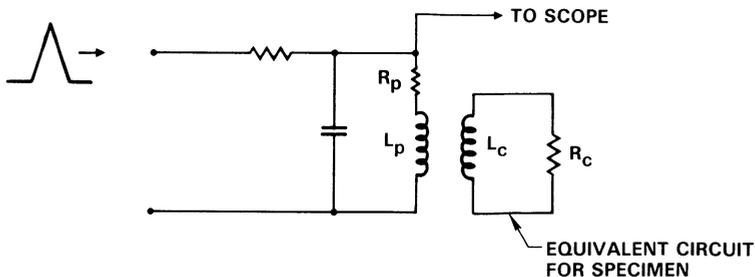

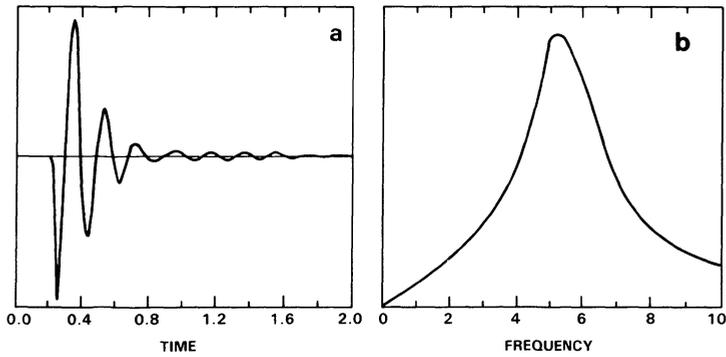Fig. 2   Model for eddy current coil and coupling to carbon-carbon specimen.

Fig. 3   (a) Damped sinusoidal signal obtained from eddy current coil. (b) Fourier transform of damped sinusoid in (a).

$$G_c = \frac{2}{\omega_0 L_c} (\zeta - \zeta_0)$$ (1)

where ζ_0 is the damping coefficient of the coil alone and ζ is the damping coefficient of the coil and specimen coupled together.

In general, the coupling coefficient of the coil to the specimen is not known so instead of absolute measurements of the conductivity, we make measurements of the relative change in the conductivity from the "as cured" state by normalizing the measured conductivity to the "as cured" value.

Initially there was some question about the reproducibility of the measurements made using this technique on a woven composite material. We needed to verify that the volume sampled by the fields from the coil was sufficiently large to give a valid average for the specimen being tested. We made measurements at room temperature of specimens cut from the same plate of material that had each been raised to a different temperature up to a maximum temperature of 700°C. We found that the normalized conductivity remained constant until a temperature of about 300°C after which it increased to about 18% more than its "as cured" value. These measurements were then repeated with a second set of specimens that had been cut from a different plate of nominally identical material. The results were identical within the measurement accuracy, thus confirming the ability of the technique to provide relative conductivities that were representative of the state of the carbon-carbon material and were not strongly dependent on the details of the composite structure such as variations in the weave or ply spacing or the position of the coil on the specimen.

COIL DESIGN

To make in situ measurements, coils were needed that would operate reliably at temperatures up to 800°C. Our current design (Fig. 4) uses a wire with an insulation that is good to 850°C. It provides sufficient space within the ceramic coil form for the coil to expand as needed with the temperature while maintaining the flat spiral geometry. A 250 μm thick alumina disk forms the side wall of the coil form and separates the coil from the carbon-carbon specimen during pyrolysis [2].

Since the electrical characteristics of the coil do change with temperature, we use two coils when making the measurements. The coils are designed to have identical electrical characteristics at room temperature. One of the coils is used
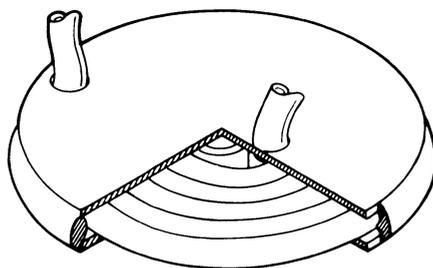
Fig. 4 Schematic of high temperature coil.

as a reference. It is placed in the same thermal environment within the retort as the measuring coil, but fields from this coil do not interact with the specimen or with the measuring coil (Fig 5). By measuring the decaying oscillation from each coil, thermal variations in the electrical properties of the coil can be compensated for and greater accuracy in the measurements of the specimen's electrical conductivity can be obtained.

EXPERIMENTAL MEASUREMENTS

These coils were used with a data acquisition system to make in situ measurements of the changes in the electrical conductivity of a 3.75 mm thick carbon-carbon specimen during pyrolysis. The pyrolysis was done in a small retort that contained a thermocouple in contact with the specimen and a pressure gauge. The retort was backfilled with Argon and the temperature was ramped up to 700°C at 100°C/hr. There was a one hour hold at 700°C before the temperature was ramped down to room temperature at 100°C/hr. The pressure was monitored and kept between 80 and 100 psi. The measured changes in the electrical conductivity are shown in Fig 6. Three data points acquired during the temperature ramp down (near 700°C) are clearly different than the others. Auxiliary measurements were used to show that the electrical properties of one of the coils changed significantly when these data points were acquired. We suspect that one or more turns of the coil may have momentarily shorted together.

In a separate experiment, a second nominally identical specimen was pyrolyzed using a temperature ramp of 25°C/hr to 700°C, a one hour hold, and a 25°C/hr ramp down to room temperature. The results of the electrical conductivity measurements are shown in Fig. 7.

DISCUSSION

The eddy current technique measures a combination of the conductivity of the graphite fibers and the conductivity of the phenolic matrix. The fibers are chemically stable and their electrical conductivity is nearly constant with temperature, whereas the phenolic matrix is being converted to carbon and its electrical conductivity is changing significantly with temperature. Probably the two conductivities suitably weighted according to the volume percent of the two materials can be treated as if they are electrically connected in parallel. Thus
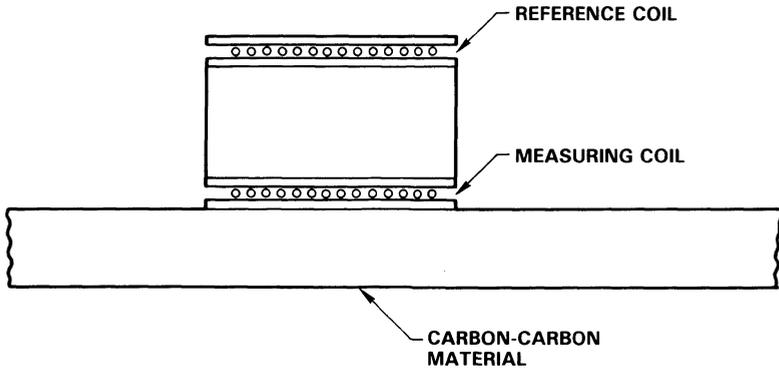
Fig. 5   Double coil technique used to compensate for thermally-induced changes in the electrical characteristics of the coil.
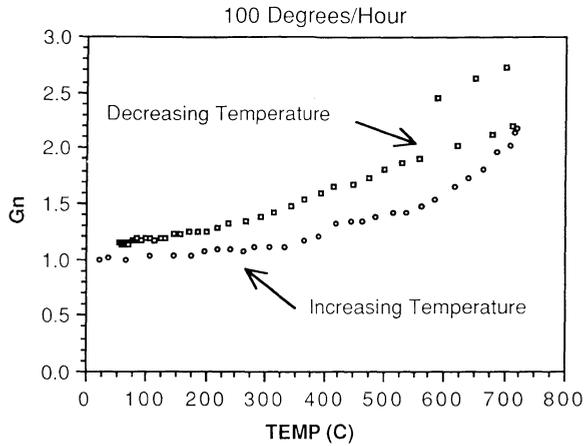

Fig. 6   In situ measurements of the changes in the electrical conductivity of a carbon-carbon specimen during pyrolysis. The temperature ramp was 100°C/hr with a 1 hr hold at 700°C.

since the conductivity of the matrix is initially orders of magnitude less than that of the fibers, the measured conductivity will display little change until the matrix conductivity becomes comparable to that of the fibers. The changes in the matrix conductivity will then be readily detectable, and the measured changes will reflect the conductivity changes in the matrix material with temperature. In addition to the chemically induced changes in the conductivity the measured conductivity will also be influenced by changes in the microstructure of the matrix such as the occurrence of cracks and porosity. These are caused by the gasses produced by the chemical reactions and by the thermal expansion mismatches between the matrix and the fibers. At the higher temperatures, the internal stresses in the material are such that the microcracks and pores are forced closed, and therefore their effect on the conductivity is minimized. When the temperature is decreased, these stresses decrease and the microcracks and pores start to open causing a significant change in the measured conductivity. Thus the increases in the conductivity that are measured as the temperature increases signify chemical changes that are carbonizing the matrix. The decreases in conductivity that are measured as the temperature decreases signify microstructural changes associated with the opening of microcracks and pores in the matrix.
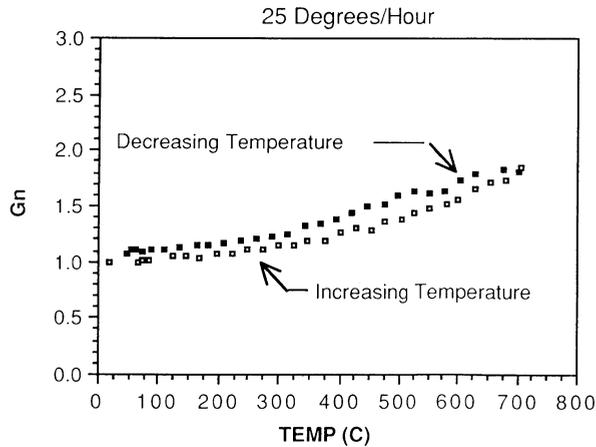
Fig. 7   In situ measurements of the changes in the electrical conductivity of a carbon-carbon specimen from the same plate of "as cured" material as that in Fig. 6. The temperature ramp was 25°C/hr with a 1 hr hold at 700°C.

The manner in which the electrical conductivity of the phenolic matrix changes with temperature is not well known. A dc resistance measurement of the resin K-641 without fibers during pyrolysis is shown in Fig. 8. The resin was heated in a pure argon atmosphere at a rate of 10°C/hr. From Fig. 8, we deduce that the conductance (the inverse of this data) starts to increase at about 150°C, reaches a local maximum at about 240°C, decreases until a temperature of 320°C, and then starts to increase in an irregular manner until about 440°C, after which it increases rapidly by eight orders of magnitude until a temperature of about 660°C is reached. It then abruptly slows its rate of increase, but continues to increase up to 800°C. Measurements by others [3] have shown that the conductivity of the carbon-carbon continues to increase until a temperature of about 2600°C has been reached at which point the carbon has been completely graphitized.

Several chemical reactions that take place during the pyrolysis of carbon-carbon contribute to changes in its electrical conductivity. The exact nature of these reactions is currently a subject of active research [4]. The first of these reactions starts at about 300°C. The hydroxyl bonds of the phenolic are converted to ether bonds and water is produced. As the temperature continues to increase, a second reaction begins at about 400°C. This reaction produces water, methane, and hydrogen, leaving a matrix of amorphous carbon. This reaction appears to be complete when a temperature of about 800°C is reached and signals the end of the carbonization of the specimen.

In comparing the data from the dc conductivity measurements and the chemical reaction measurements, we observe that the initial changes in the electrical conductivity of the phenolic are difficult to explain although some of them seem to correlate with the first chemical reaction. The rapid increase in conductivity of 8 orders of magnitude that starts at about 440°C seems to correlate with the second reaction. We believe that the abrupt change in the rate of increase of the conductivity that is observed after 660°C may occur because the phenolic has been completely carbonized. The slower rate of increase above 660°C/hr is probably caused by changes in the morphology of the carbon as it starts to form polymer chains and begins its conversion to graphite. It is puzzling that this does not occur after the completion of the carbonization rather than at 660°C.
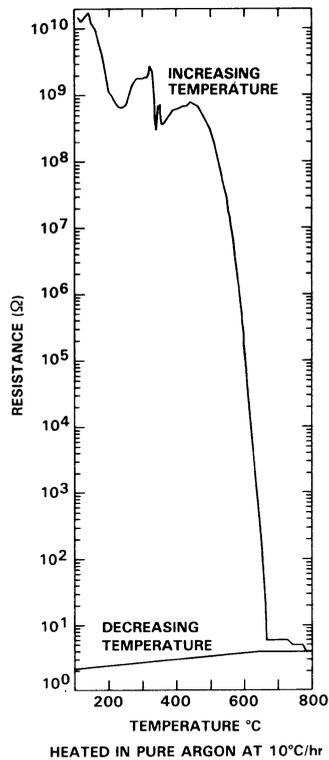
Fig. 8 DC resistance measurement of the resin K-641 without fibers during pyrolysis in pure argon at 10°C/hr. (Data courtesy of C.S. Hollingsworth.)

The eddy current conductivity data (Figs. 6 and 7) probably does not detect the small changes in electrical conductivity that occur in the 200-450°C range because the phenolic conductivity is orders of magnitude less than that of the fibers. For temperature increases beyond 450°C, the eddy current data starts to increase rapidly consistent with the rapid change in the conductivity measured in the phenolic. Since we do not observe any abrupt change in the rate of increase of the measured conductivity at 660°C in Fig. 6, it may mean that the carbonization was not complete at 700°C. This would be consistent with the experiment that measured the evolution of gasses and showed that it was not complete until 800°C. On the other hand, the data in Fig. 7 does appear to be leveling off in the 600-650°C range. However the relative change in the electrical conductivity from the "as cured" value is less than that observed for the more rapid heating rate. These differences cannot be explained from the observations that have been made thus far. Additional experiments that systematically measure the differences in the conductivity vs heating rate are necessary. In addition, further postprocessing analysis of the relative mixture of the amorphous and polycrystalline carbon present in the specimens is needed.

The decrease in the conductivity that is observed (Figs. 6 and 7) as the temperature decreases is attributed to the opening of microcracks in the carbonized matrix material. The limited data acquired thus far does not permit many generalizations to be made about this decrease. We observe that the rate of decrease seems to be somewhat higher at the higher temperatures for the data in Figs. 6 and 7. The room temperature conductivity of the carbonized specimens is higher than the "as cured" value by about 15-20%. This value seems to be proportional to the maximum conductivity reached during the pyrolysis. Some variations observed in the curves seem to be specific to each specimen and may be

associated with the details of the microstructure of a specific specimen. We are not able to interpret this yet.

CONCLUSIONS

These experiments are considered to be preliminary, but do demonstrate that this method of making in situ measurements of the electrical conductivity of the carbon-carbon during processing is a feasible technique for observing changes in the material. To make this technique more useful, we plan to extend the measurements to include the imaginary part of the conductivity, i.e., we will measure the complex admittance of the specimen. This will allow changes in the polarizability of the matrix to be deduced, and thus will provide a potentially rapid technique for local monitoring of the progress of the chemical reactions. We also intend to make measurements at different frequencies to obtain information about the variation of the complex admittance with depth. This will allow the monitoring of variations in the rate of the chemical reactions with depth and will provide valuable data for adjusting the rate of pyrolysis to maximize the rate of increase of the temperature while minimizing the probability of delamination.

ACKNOWLEDGEMENTS

REFERENCES

1. W.J. Pardee, J. Bulau, R.C. Addison, and K. Chung, "Sensors For Carbonization Control," in Review of Progress in Quantitative Nondestructive Evaluation, ed. D.O. Thompson and D.E. Chimenti, vol. 8B, pp. 1185-1193, Plenum Press, New York, 1989.
2. We acknowledge the help and advice of G.A. Alers at Magnasonics with the initial design of the high temperature coils.
3. J. Delmonte, Technology of Carbon & Graphite Fiber Composites, pp. 251-269, von Nostrand, New York, 1981.
4. W.J. Pardee, M.R. Mitchell, A. Gupta, F. Montgomery, and J. Sheehan, Effect of Carbonization Kinetics on In-Process Mechanical Properties, to be presented at the Fall 1989 TMS Meeting.